

NOVEL LOW-TEMPERATURE POSS-CONTAINING SILOXANE ELASTOMERS

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ABSTRACT

One route to increased aircraft performance is through the use of flexible, shape-changeable aerodynamics effectors. However, state of the art materials are not flexible or durable enough over the required broad temperature range. Mixed siloxanes were cross-linked by polyhedral oligomeric silsesquioxanes (POSS) producing novel materials that remained flexible and elastic from -55 to 94 °C. POSS molecules were chemically modified to generate homogeneous distributions within the siloxane matrix. High resolution scanning electron microscope (HRSEM) images indicated homogenous POSS distribution up to 0.8 wt %. Above the solubility limit, POSS aggregates could be seen both macroscopically and via SEM (~60-120 nm). Tensile tests were performed to determine Young's modulus, tensile strength, and elongation at break over the range of temperatures associated with transonic aircraft use (-55 to 94 °C; -65 to 200 °F). The siloxane materials developed here maintained flexibility at -55 °C, where previous candidate materials failed. At room temperature, films could be elongated up to 250 % before rupturing. At -55 and 94 °C, however, films could be elongated up to 400 % and 125 %, respectively.

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INTRODUCTION

Three specific techniques for improving mechanical properties in elastomers include forming bimodal networks, using bulk fillers, and altering the cross-link chemistry with a reinforcing agent. A bimodal network is comprised of polymer components with two different chain-length distributions. A network composed of short and long chains is typically observed to have a high ultimate strength without compromising maximum elongation [1]. Previous research using bulk microscopic fillers as reinforcement, such as silica or carbon black, showed high ultimate strength and high elongation at break. However, the highly viscous polymers generated by this technique are cumbersome to process [2]. While an abundance of literature exists on polymers

containing polyhedral oligomeric silsesquioxanes (POSS) [3], POSS has primarily been used as a non-covalent polymer filler [4], pendant [5], or in-backbone modifier [6] where its use improved a variety of physical, thermal, and mechanical properties [7].

In this work POSS molecules were incorporated as novel cross-linking agents (Figure 1) into flexible siloxane networks in an effort to enhance their tensile properties from -55 °C to 94 °C. These nanoscale molecules were chosen because they have a well-defined structure, silica-like core (e.g. Si₈O₁₂), and, in the case of Si₈O₁₂, eight organic groups at the corners of the cube (see inset of Figure 1). Functional corner groups like vinyl, for example, enable POSS to be reacted with other molecules and thus they can be used to covalently reinforce a polymer network. It was envisioned that covalent POSS incorporation would provide a greater degree of polymer matrix reinforcement compared to non-covalent incorporation and thus greater mechanical properties enhancement [8].

EXPERIMENTAL SECTION

Materials. Octavinyl-polyhedral oligomeric silsesquioxane (octavinyl-POSS) was used as received from Hybrid Plastics (Hattiesburg, MS). Vinyl terminated (35-45% trifluoropropylmethylsiloxane)-(65-55% dimethylsiloxane) copolymer (FMV-4031; referred to as “trifluoro component”), trimethylsiloxane terminated (25-30% methylhydrosiloxane)-(75-70% dimethylsiloxane) copolymer (HMS-301; referred to as “hydromethyl component”), and diethylsilane (SID3415.0) were used as received from Gelest, Inc. (Tullytown, PA). Platinum (0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.05 M solution in vinyl terminated polydimethylsiloxane; also called Karstedt’s catalyst) was used as received from Aldrich (Milwaukee, WI). [See Figure 2.] Methylene chloride was used as received from Fisher Scientific (Pittsburgh, PA).

General Preparation Procedure. Octavinyl-POSS was chemically modified (see Figure 3) to afford covalent incorporation into the siloxane network (see Figure 4) comprised of ~30 % diethylsilane, ~60 % trifluoro component, ~8 % hydromethyl component and variable amounts of both octavinyl-POSS and Karstedt’s catalyst. More specifically, octavinyl-POSS (from 0 to 1 wt %) was dissolved in a minimal amount of methylene chloride. Diethylsilane and Karstedt’s catalyst (0.6 to 1.2 wt %) were added and the mixture was stirred by hand. After ~30 s the trifluoro component was added with stirring until the reaction mixture was a uniform consistency followed by addition of the hydromethyl component and further stirring. After all the components were stirred for ~60 s, the reaction mixture was poured into non-stick perfluoroalkoxy (PFA) resin dishes (Savillex Corporation). Individual bubbles in the wet film were popped using minimal pressure from a pressurized air canister. Films were cured at room temperature overnight and were subsequently heated in a drying oven at 60 °C for a few hours. After curing, films were peeled from the PFA dishes and die-cut into Type V specimens (ASTM Standard D 638-02a).

Characterization. Individual specimens were analyzed in several ways. Scanning electron microscopy (SEM) images were collected on a Hitachi S-5200 Field Emission High Resolution Scanning Electron Microscope equipped with a through the lens (TTL) detector. Differential scanning calorimetry (DSC) was completed on a DSC Q100

Differential Scanning Calorimeter by TA Instruments (-80 to 300 °C at 20 °C/min). Thermal gravimetric analysis (TGA) was completed on a TGA Q500 Thermogravimetric Analyzer by TA Instruments under an atmosphere of air (25 to 100 °C at 20 °C/min, hold 30 min, then 2.5 °C/min to 700 °C). Coefficient of thermal expansion (CTE) was determined per sample on a TMA Q400 Thermomechanical Analyzer by TA Instruments (2 °C/min from -60 to 250 °C).

Tensile Testing. Prior to mechanical testing, the thickness of each individual specimen was measured using either a digital caliper (Mitutoyo Corporation) or micrometer (Precision Micrometer, Testing Machines, Inc.), depending on overall thickness, which ranged from ~0.6 to ~1.0 mm. Each sample was then installed on a test stand (Sintech) with a 1" gauge length between self-tightening roller grips (Instron) with a universal joint in the load train. An SMT 1-11 lb load cell (Interface, Inc.) was used to determine load. Elongation was estimated using the crosshead displacement. For each tensile test, the load and elongation data was collected using MTS Corporation TestWorks 4 software. For the tests conducted at non-ambient conditions, a Thermcraft, Inc. oven with a solenoid valve coupled to a liquid nitrogen Dewar was employed. A second digital thermometer (Fluke 2170A) was used to verify the chamber temperature. Once the temperature of the grips and sample reached equilibrium, typically after 10 min, each specimen was stretched at a rate of 7.5 in/min up to the moment of rupture, at which point the elongation at break, strain at break, and break load were recorded for later analysis.

RESULTS AND DISCUSSION

Direct incorporation of octavinyl-POSS into the proposed novel siloxane network was unsuccessful due to phase separation of the crosslinking agent and the unreacted matrix components. To improve compatibility with the siloxane network, octavinyl-POSS was chemically modified *in-situ* with diethylsilane (Figure 3). The pre-treated reinforcing agent is likely comprised of a distribution of differing degrees of functionality, from zero to eight chemically modified corners. HRSEM photomicrographs of some characteristic siloxane film samples are shown in Figure 5. The 0.3 wt % POSS film revealed no incongruities (Figures 5a and b), meaning no POSS aggregation, on either the surface (save for some apparent bubbles) or in the cross-sectional portion (the rough textured portion at the right of Figure 5a). Similarly, at 0.7 wt % POSS, no aggregation on either the surface or at any specimen cracks is observed (Figures 5c and d). However, at 1.2 wt % POSS, surface irregularities ~60-120 nm in size appear (Figures 5e and f), indicating that the matrix is over the POSS solubility limit, which is estimated to be 0.9 wt %. Therefore, only materials near or below the solubility limit (\leq 1 wt % POSS) were used for further studies.

Variation of POSS content from 0 to 1 wt % resulted in minimal change in the thermal properties of these elastomers. DSC traces did not indicate distinct melting peaks (T_m) or glass transitions (T_g) for any sample. Table 1 shows TGA and CTE data relative to POSS content. TGA showed all samples to be thermally stable up to 100 °C followed by a gradual loss in mass to 350 ± 3 °C (T_{d10} , temperature by which 10 % of the material had been lost). It was expected that CTE values for the reinforced films would decrease

with increasing POSS content. A 0 wt % POSS sample would have the largest CTE value, corresponding with greater elongation and apparent higher flexibility. As POSS content increased, CTE values should decrease, reflecting an increase in crosslink density and thus higher rigidity. However, preliminary data do not show the expected trend and overall the CTE values were higher than anticipated.

Table 1. TGA and CTE data relative to POSS content

POSS Content (wt %)	T _{d10} (°C)	CTE [$\mu\text{m}/(\text{m}\cdot^\circ\text{C})$]
0	347	843
0.2	348	934
0.4	347	918
0.6	348	626
0.8	349	870
1.0	353	666

Figure 6, a plot of Young's modulus versus POSS content, shows a direct relationship between polymer reinforcement and Young's modulus values at -55 and 23 °C, yielding up to ~60 % improvement at room temperature and ~30 % improvement at the lower temperature. At 94 °C, however, the opposite trend is observed with up to a ~60 % decrease in Young's modulus. Figure 7 shows a slight decrease in tensile strength with added polymer reinforcement at room temperature and a drastic decrease at low temperature. At high temperature, however, a very subtle increase in tensile strength was observed.

Dependence of elongation at break on POSS content is shown in Figure 8. Of greatest significance for these results is that the POSS-reinforced elastomers remained flexible at -55 °C. That these samples exhibited greater elongation before failure than those tested at room temperature or 94 °C by a factor of about 2 was quite interesting and might be explained by a delay in stretching of polymer network chains or slower chain motion due to the low temperature [9]. At all temperatures tested elongation was lower at higher POSS loadings, as could be expected.

These novel elastomers exhibited a noticeable decrease in temperature dependence of the observed mechanical properties (Figures 6-8) for samples with intermediate POSS loadings (0.4 – 0.6 and in some cases 0.8 wt %). These results suggest that incorporation of POSS into the siloxane network, at least at these loadings, yields thermal stabilization of mechanical properties while still providing desired changes in the behavior of the material (i.e., increased durability and flexibility over an expanded temperature range).

CONCLUSIONS

Octavinyl-POSS was employed as a covalent, nanoscale molecular reinforcement (i.e., not as a filler) to create novel siloxane systems. POSS content was varied to allow for a systematic study. Mechanical testing was done to determine the additive's effect on Young's modulus, tensile strength, and elongation at break of the novel reinforced polymers reported here. Data analysis indicated a positive correlation between POSS content and Young's modulus, yielding up to 50 % improvement at room temperature.

However, negative correlations were observed for both elongation at break (up to 50 % decrease) and tensile strength (up to 65 % decrease). The structure/property relationships shown in Figures 6-8 may prove useful in considering future formulations, including work with films containing intermediate POSS content, particularly in the 0.3 to 0.7 wt % range. Comparing collected mechanical property values with theoretical predictions concerning effective chain length and crosslinking density correlations with modulus and elongation are also of interest. It is worth noting that the materials developed, tested, and reported here remained flexible at -55 °C whereas previously considered and developed materials failed to meet this requirement, instead becoming brittle at -55 °C. It is also of interest that these materials exhibited greater elongation at -55 °C than at room temperature.

ACKNOWLEDGEMENTS

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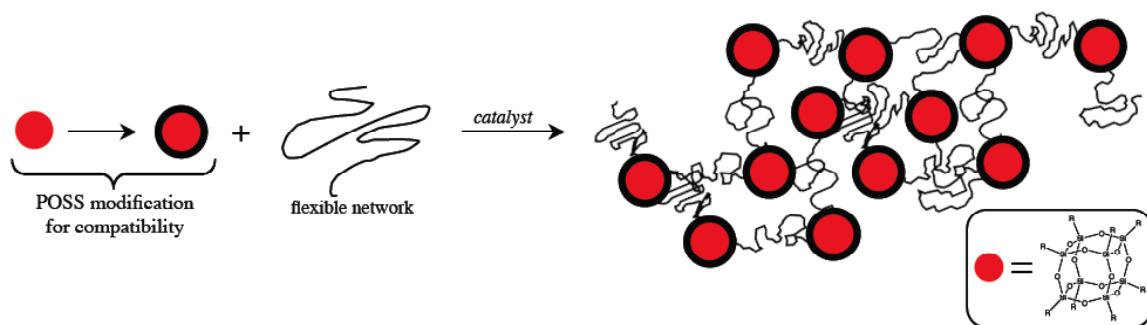


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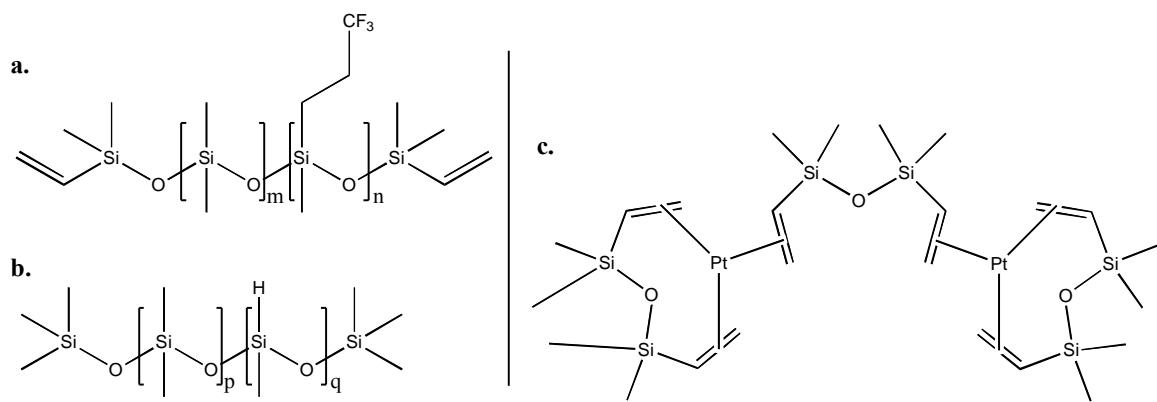


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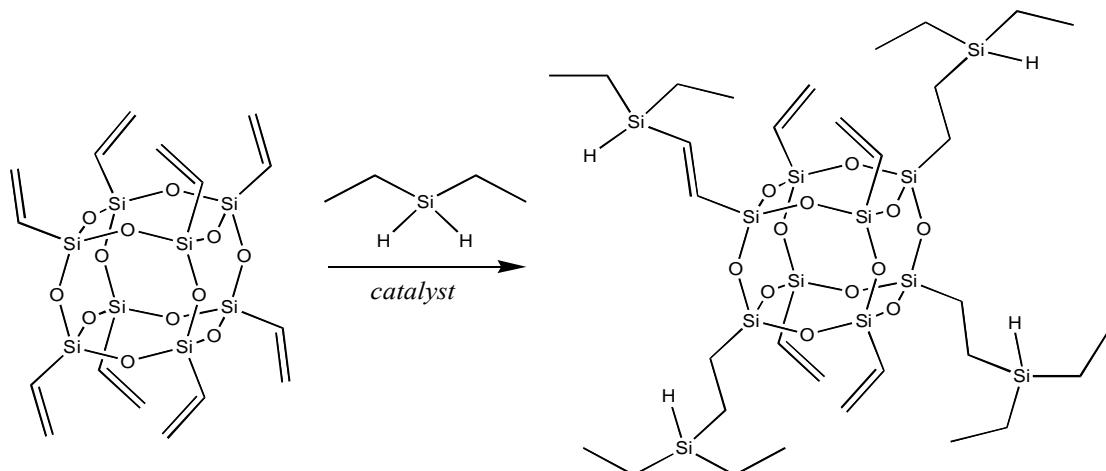


Figure 3. Chemical modification of octavinyl-POSS (product shown with four diethylsilyl functionalities for illustrative purposes)

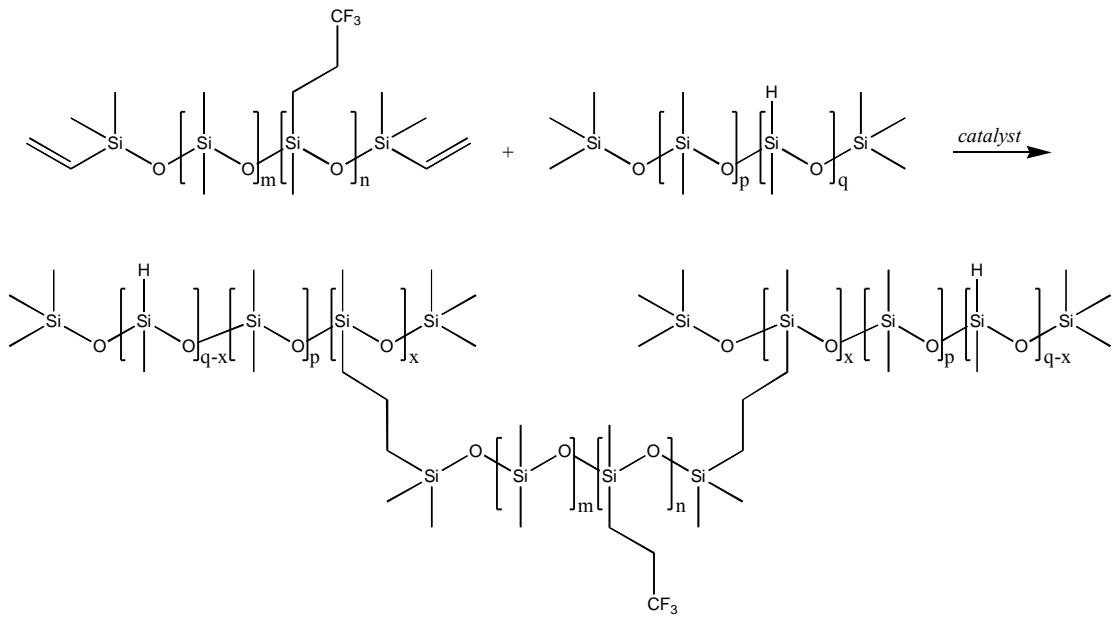
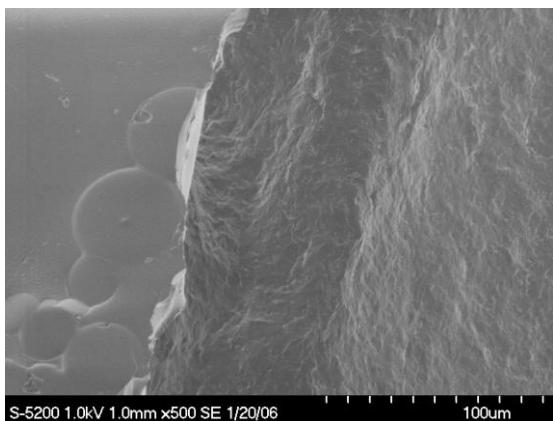
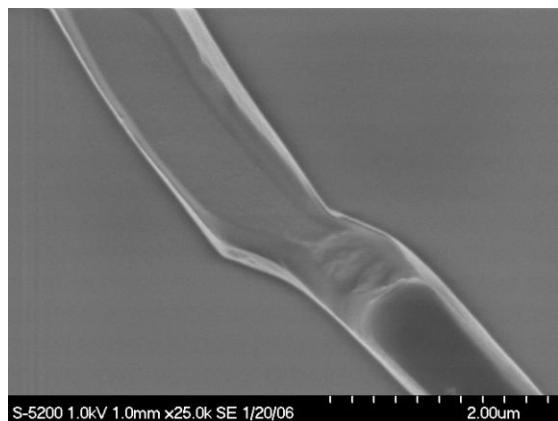


Figure 4. Simplified network formation (0 % POSS shown)



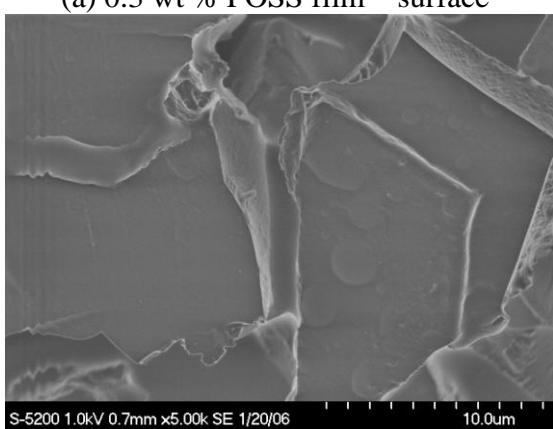
S-5200 1.0kV 1.0mm x500 SE 1/20/06

(a) 0.3 wt % POSS film – surface



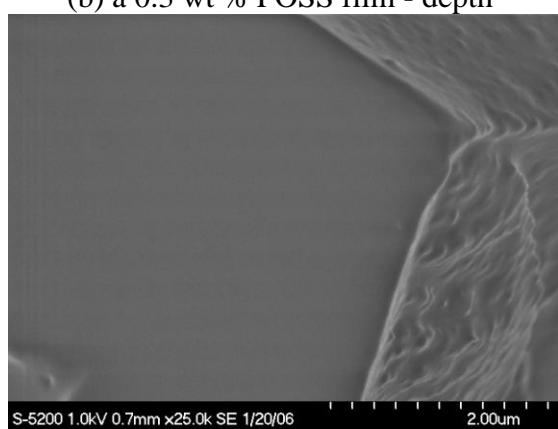
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(b) a 0.3 wt % POSS film - depth



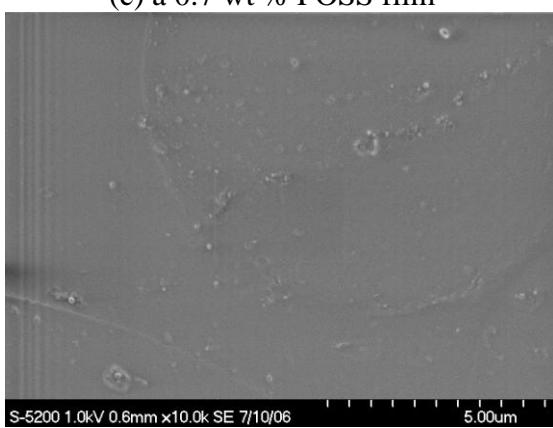
S-5200 1.0kV 0.7mm x5.00k SE 1/20/06

(c) a 0.7 wt % POSS film



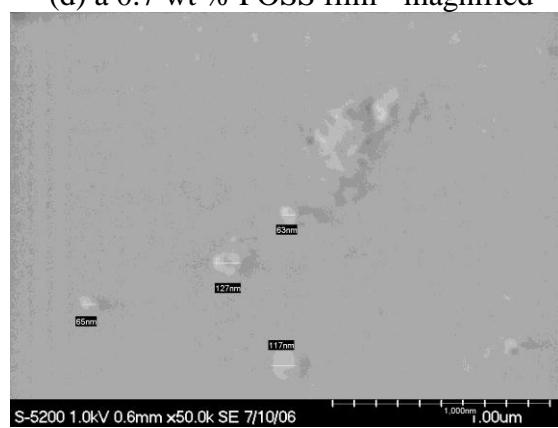
S-5200 1.0kV 0.7mm x25.0k SE 1/20/06

(d) a 0.7 wt % POSS film - magnified



S-5200 1.0kV 0.6mm x10.0k SE 7/10/06

(e) sample with 1.2 wt % POSS



S-5200 1.0kV 0.6mm x50.0k SE 7/10/06

(f) sample with 1.2 wt % POSS - magnified

Figure 5. High Resolution Scanning Electron Microscope (HRSEM) photomicrographs of some characteristic siloxane film samples

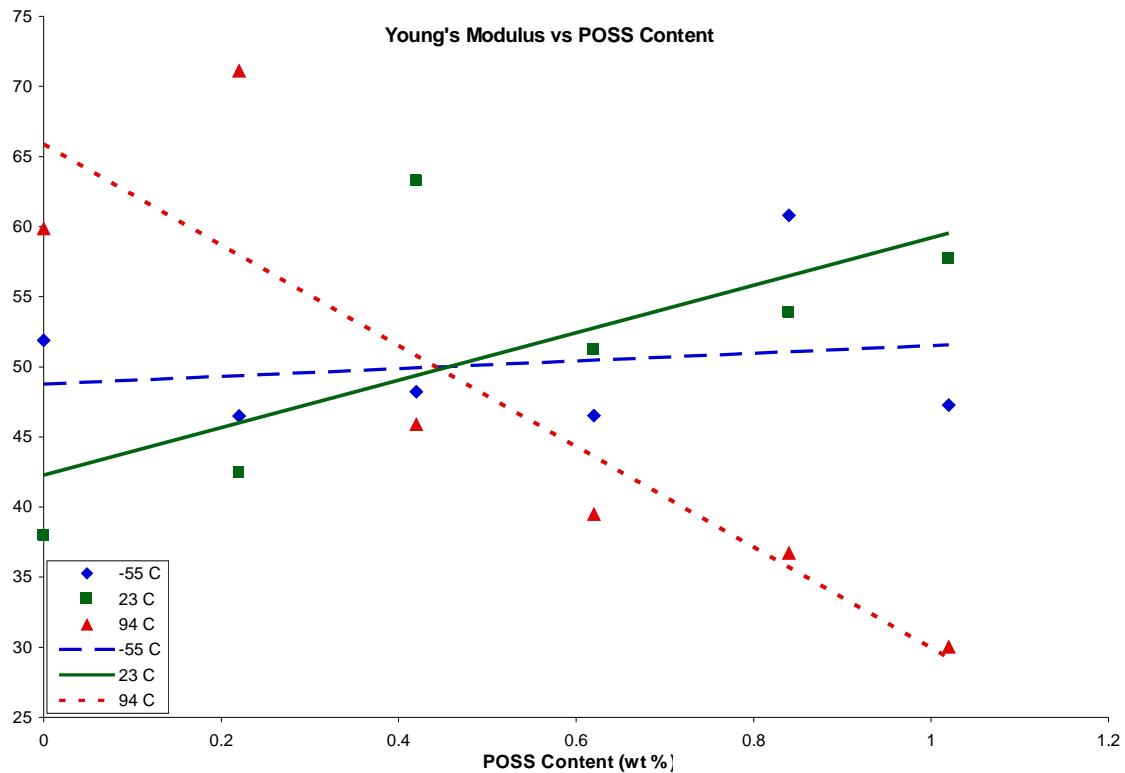


Figure 6. Young's modulus vs. POSS content

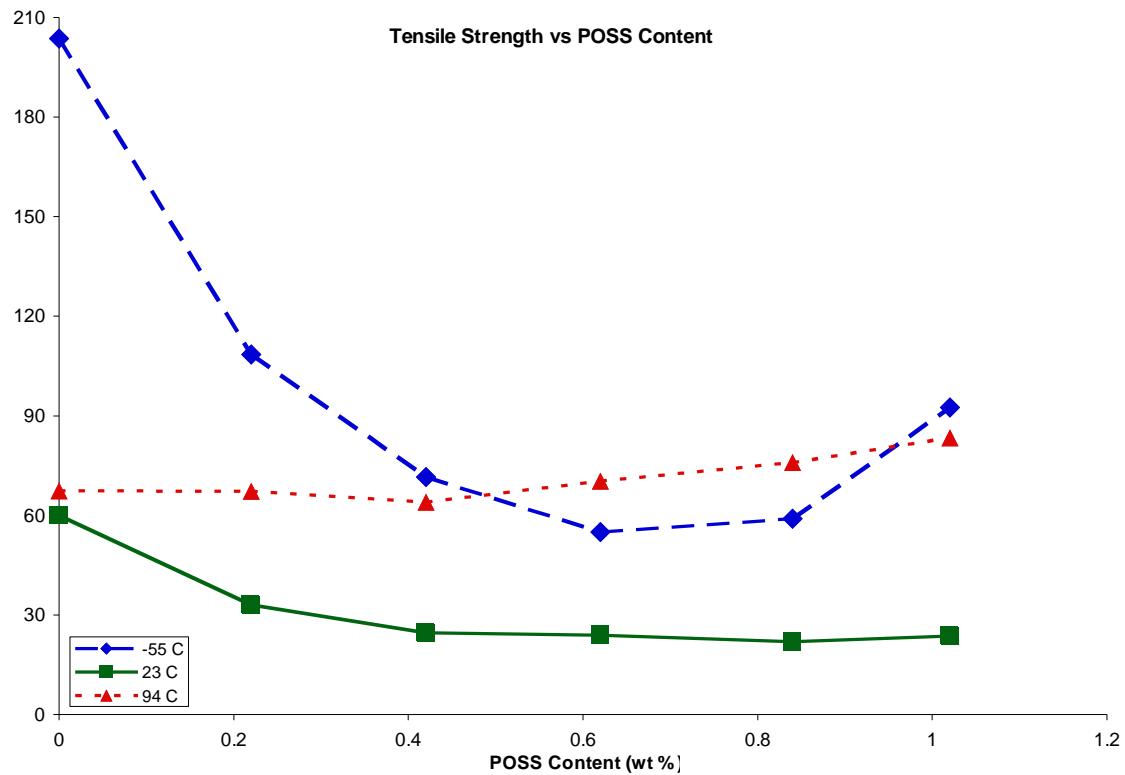


Figure 7. Tensile strength vs. POSS content

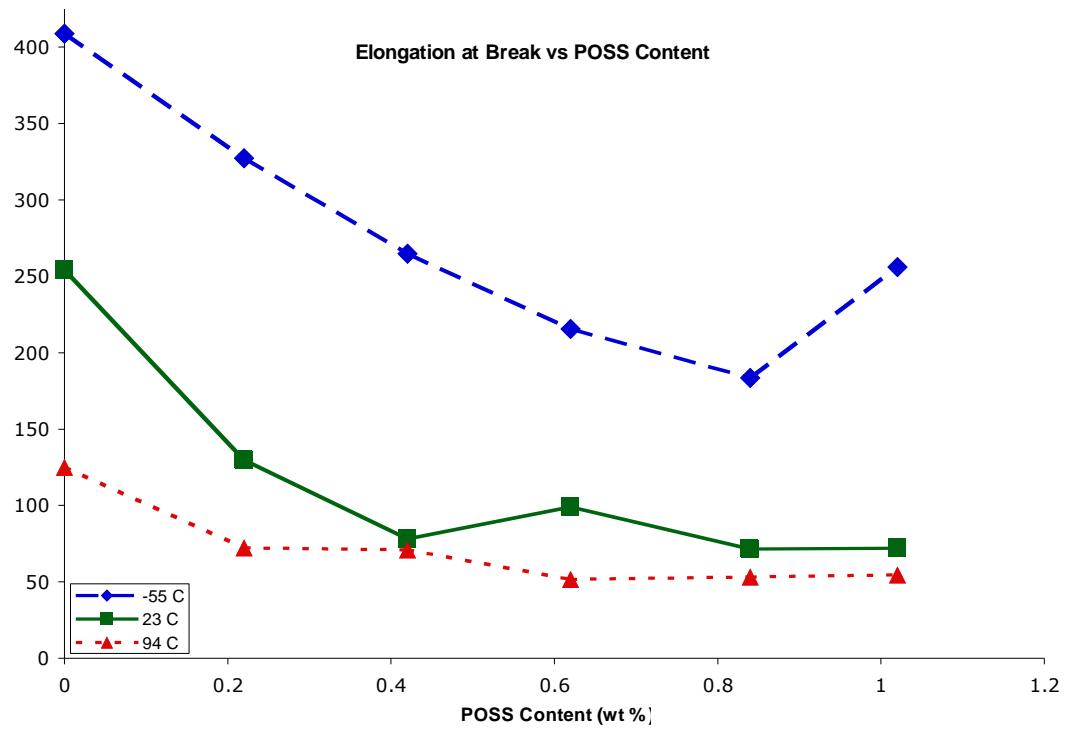


Figure 8. Elongation at break vs. POSS content